

Analysis of Trace Sulfur Compounds in Beverage Grade Carbon Dioxide Application

Gas Chromatography

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Abstract

An inert valving system using the volatiles interface (VI) on the Agilent 6890 is described for the analysis of ppb level volatile sulfur compounds in food grade carbon dioxide. Examples using the Agilent AED, FPD, and Sievers SCD are shown. The blending of CO₂ with an eight component sulfur mix provides an easy to use means of calibrating the system for low level sulfur determinations.

Introduction

The food and beverage industry has strict guidelines on the quality of CO₂ required for use in products for human consumption. Food grade CO₂ (> 99.95%) can contain a number of impurities. Impurities can produce off-odors or flavors and in some rare instances a health hazard can result. Guidelines¹ have been established recently for allowable levels of impurities by chemical type. These have been published by the International Society of Beverage Technologists (ISBT).

The most common impurities are acetaldehyde, methanol, ethanol, hydrogen sulfide, carbonyl sulfide, and sulfur dioxide. For example, the guideline concentrations for total sulfur and total volatile hydrocarbons is 0.1 ppm v/v and 50 ppm v/v, respectively. A chromatographic system based on the Agilent 6890 equipped with a sulfur selective detector can easily quantify sulfur at levels well below those recommended for food grade CO₂. Strict adherence to sample introduction hardware recommendations is required for reliable operation.



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Experimental

The sulfur selective detectors (one per GC) were mounted on the Agilent 6890 gas chromatograph equipped with the volatiles interface. The GC was configured for 220 V operation in order to achieve high oven ramp rates. All GC gas flows and pressures were controlled electronically. A 6-port gas-sampling valve (GSV) in Hastelloy C was interfaced directly to the Silcosteel treated VI with 1/16-inch Silcosteel tubing, Restek part no. 20595. All lines coming in contact with the sample including the 1 cc sample loop were Silcosteel treated to provide inertness necessary for low level sulfur analysis. A diagram of the sample introduction system is shown in Figure 1.

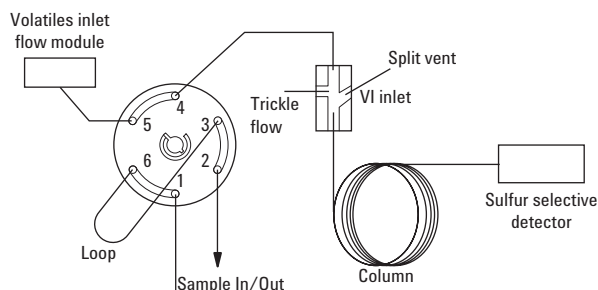


Figure 1. Sample introduction system.

All samples were introduced to the GC in the gas phase. Chromatographic conditions employed are given below.

Gas sampling valve:	1 cc loop at 140 °C, Hastelloy C material
Column:	105 m × 0.53 mm × 5 µm DB-1
Typical oven:	-20 °C (9.5 min), 10 °C/min to 250 °C, 80 °C/min to 280 °C
VI Inlet:	5 mL/min, constant flow mode Temp 150 °C, Split ratio 0.1:1

A dynamic blending system was used to add sulfur calibration mix, in a controlled fashion, to the pure CO₂ matrix, producing a stream of known sulfur concentrations for delivery to the GSV. This system is shown in Figure 2. The sulfur calibration mix (DCG Partnership I, LTD., Pearland, TX, 281-648-1894) consisted of the components listed in Table 1 at certified concentration levels of 5 ppm each.

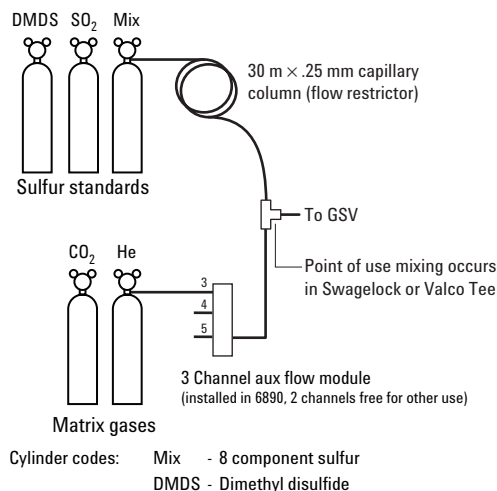


Figure 2. Dynamic blending scheme.

Table 1. Sulfur Mix Components

Number	Compound
1	Hydrogen sulfide
2	Carbonyl sulfide
3	Methyl mercaptan
4	Ethyl mercaptan
5	Dimethyl sulfide
6	Carbon disulfide
7	t-Butyl mercaptan
8	Tetrahydrothiophene

The AED, FPD, and Sievers SCD (Sulfur Chemiluminescent Detector) were used in the study. For maximum sensitivity, the FPD was setup in hydrogen rich mode. Detector conditions are shown in Table 2.

Table 2 Detector Settings

Detector	Temperatures	Pressures and Flows
Agilent Flame Photometric	250 °C	H ₂ 50 mL/min Air 60 mL/min N ₂ makeup 50 mL/min
Agilent G2350A Atomic Emission Sulfur 181 nm	Cavity 245 °C Transfer line 245 °C	O ₂ 55 psi H ₂ 45 psi He makeup 100 mL/min
Sievers 355 Sulfur Chemiluminescent	803 °C Furnace	P1 5.4 Detector P2 171 Furnace H ₂ 100 mL/min O ₂ 8 mL/min O ₃ 5.6 psi

Results

The FPD demonstrated excellent sensitivity to a 25 ppbv/component sulfur mix in pure CO₂ as shown in Figure 3. This level of sample mix was prepared using the dynamic blending system by

mixing 1 mL/min sulfur calibration standard with 199 mL/min CO₂. Quantitation of all components except for H₂S is possible at this level. Hydrogen sulfide at levels of approximately 50 ppbv should be quantifiable with the FPD when using the sample introduction system described here.

In Figure 4, AED chromatograms of the sulfur 181 nm line are shown at sulfur mix concentrations of 5 ppm (no dilution) and 35 ppb (dilution in CO₂). All eight sulfur compounds show good signal to noise at the 35 ppb level.

Next, pure CO₂ was analyzed without addition of the sulfur calibration mix. Care was taken to ensure that carryover of residual sulfur compounds was not mistakenly identified as

components present in the CO₂. Helium was used to purge the lines thoroughly for approximately 1 hour. Injections of helium were made into the GC-AED system to monitor any potential carry-over. It is not uncommon to see residual levels of some sulfur mix compounds present for one or two GSV injections after the mix is disconnected.

Figure 5 shows a SCD chromatogram of pure CO₂ blended with the sulfur mix to 25 ppb. The SCD was able to detect down to levels of approximately 2 ppb for COS when using a 5 mL sample loop. Carbonyl sulfide and carbon disulfide in pure CO₂ can be seen at levels of 2 ppb and 1 ppb, respectively, on the AED in Figure 6.

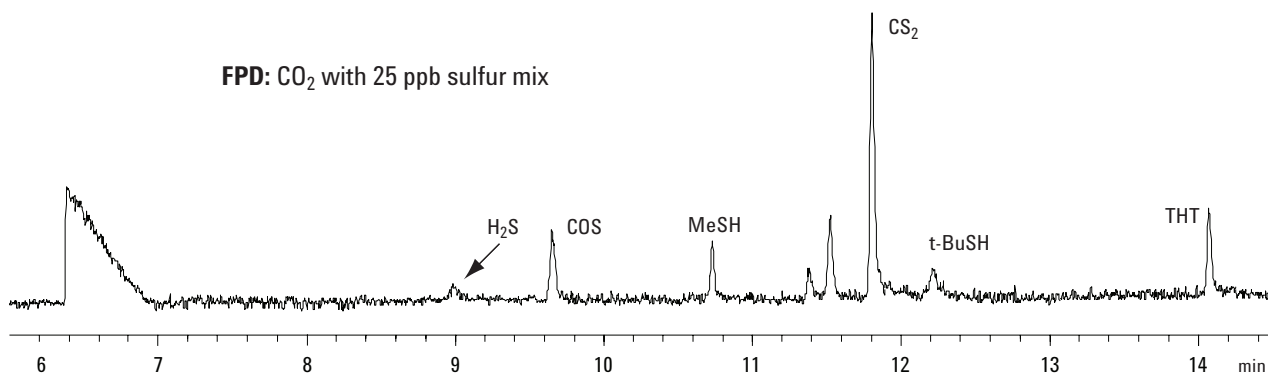


Figure 3. Carbon dioxide with 25 ppb sulfur calibration mix. Detector: Agilent Flame Photometric. One cc sample loop, no split.

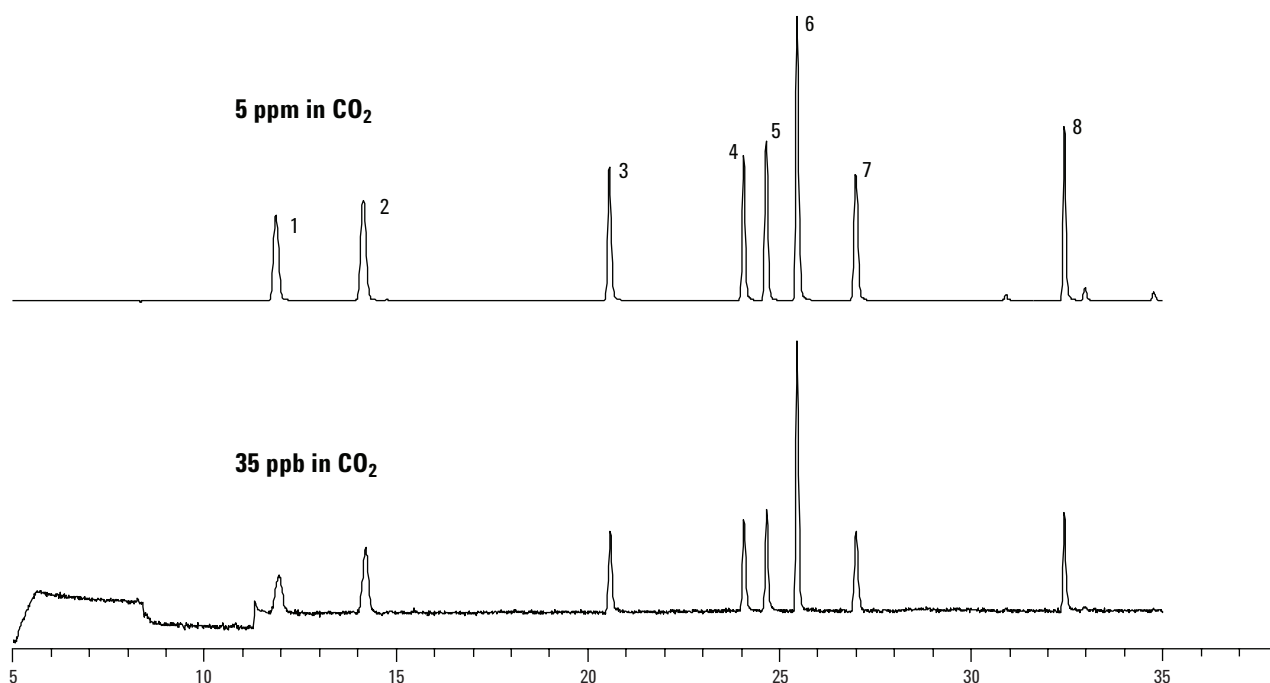


Figure 4. Sulfur calibration mix in CO₂ at levels of 5 ppm and 35 ppb. Detector: Agilent Atomic Emission.

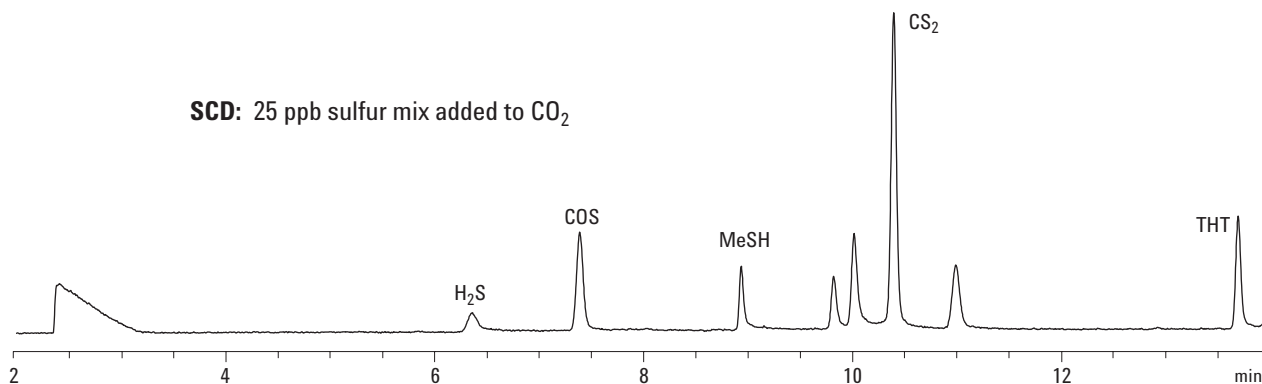


Figure 5. Analysis of food grade CO₂. Detector: Sievers SCD.

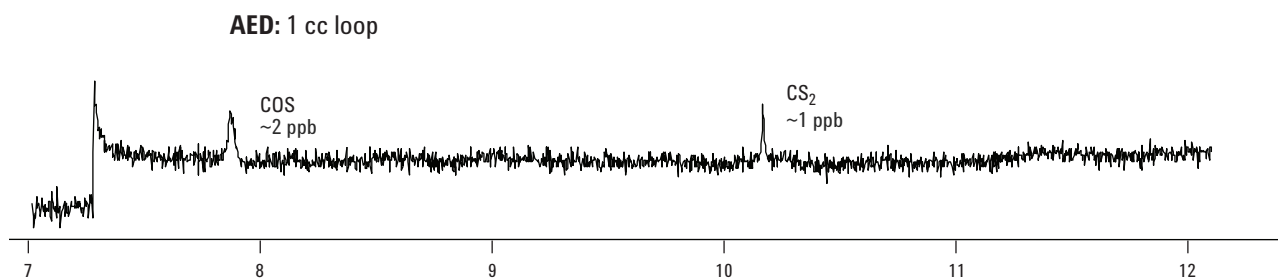


Figure 6. Analysis of food grade CO₂. Detector: Agilent AED.

A number of non-sulfur impurities can also be present as outlined in the ISBT guide. Although not shown in this application note, the AED could be used to look at the S 181 nm and C 193 nm lines simultaneously. Thus, many of the hydrocarbon impurities could easily be separated and quantified at low ppb levels using the 105 m × 0.53 mm × 5.0 µm DB1 column in an Agilent 6890/AED system. The carbon 193 nm line is approximately five times more sensitive than the FID for those compounds that respond well on a FID. Therefore detectability of the hydrocarbon impurities would not be difficult at the levels required.

Conclusions

For detection of sulfur impurities in beverage grade CO₂ at levels down to 25 ppb, the FPD offers an easy-to-use low cost solution when coupled to the optimized sample introduction system presented here. The sulfur chemiluminescent detector (SCD) offers better sensitivity at a higher

cost and somewhat more difficult setup/tuning compared to the FPD. The AED offers the most complete solution when analysis of hydrocarbons is also desired with a single valve-column-detector combination.

References

1. Carbon Dioxide Quality Guidelines and Analytical Procedure Bibliography, International Society of Beverage Technologists, Homosassa, FL, (1999)

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